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## DETAILED DESCRIPTION

### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the manufacture method of of the ferroelectric random-access memory and ferroelectric random-access memory which can be driven by the low battery while carrying out orientation of the crystal face of a ferroelectric film and obtaining a high remanence value and a high SN ratio especially about the manufacture method of the suitable ferroelectric memory for a nonvolatile semiconductor device, and ferroelectric random-access memory.

[0002]

[Description of the Prior Art] Conventionally, there is ferroelectric memory (FeRAM; Ferroelectric Random Access Memory) which used the ferroelectric as a capacitor insulator layer. Drawing 6 is the cross section showing the composition of the 1st conventional ferroelectric random-access memory, drawing 7 is the cross section showing the 2nd conventional ferroelectric random-access memory, and drawing 8 is the cross section showing the 3rd conventional ferroelectric random-access memory.

[0003] As the 1st conventional ferroelectric random-access memory is shown in drawing 6, SiO<sub>2</sub> film 101 whose thickness is 5000Å is formed on the semiconductor substrate 100 which consists of Si. On this SiO<sub>2</sub> film 101, the Pt film 102 the main orientation was carried out [ the film ] to the field whose thickness is 1000Å (111) by sputtering etc. is formed. The PZT (Pb(Zr, Ti) O<sub>3</sub>) film 103 by which the main orientation was carried out to the field whose thickness is 2000Å (111) is formed on this Pt film 102. The Pt film 104 by which the main orientation was carried out to the field whose thickness is 1000Å (111) is formed on this PZT film 103.

[0004] Moreover, as compared with the 1st conventional ferroelectric random-access memory, the films formed among the Pt films 102 and 104 differ at the point which is the SBT (SrBi<sub>2</sub>Ta 2O<sub>9</sub>) film 105, and the 2nd conventional ferroelectric random-access memory is the same composition as the 1st conventional ferroelectric random-access memory except it, as shown in drawing 7.

[0005] furthermore, the front face which consists of MgO as the 3rd conventional ferroelectric random-access memory is shown in drawing 8 -- the semiconductor substrate 100a top of a field (100) -- thickness -- 1000Å -- it is (100) -- Pt film 102a by which orientation was carried out is formed On this Pt film 102a, PZT film 103a by which orientation was carried out is formed in the field whose thickness is 2000Å (001). On this PZT film 103a, Pt film 104a by which orientation of the thickness was carried out to the field (111) by 1000Å is formed.

[0006]

[Problem(s) to be Solved by the Invention] However, in the 1st conventional ferroelectric random-access memory, the self-stacking tendency of Pt film is strong, and when the Pt film 102 is formed, a front face usually tends to turn into a field (111). It is easy to carry out orientation of the PZT film 103 formed on the Pt film 102 by which orientation was carried out to this (111) field to a field (111) or (100) a field, and orientation is hardly carried out to a field including a polarization shaft (001). For this reason, as compared with the PZT film of the single crystal by which orientation was carried out to the field (001), there is a trouble that the remanence value Pr turns into a low value. Moreover, there is a trouble that the

remanence ratio of a hysteresis curve is small and the SN ratio at the time of polarization reversal becomes low.

[0007] Furthermore, there is a trouble that it is difficult for the saturation characteristics over the voltage of this hysteresis curve to drive by the low battery bad.

[0008] Moreover, the 2nd conventional ferroelectric random-access memory is excellent in the remanence ratio of a hysteresis curve, and has the trouble that the remanence value  $P_r$  of what can acquire the hysteresis saturated with a low battery is  $1/2$  or less [ of a PZT film ].

[0009] Moreover, there is a trouble that the annealing temperature at the time of manufacture needs to make it higher than a PZT film.

[0010] Furthermore, the 3rd conventional ferroelectric random-access memory can obtain PZT film 103a of the single crystal of a field on Pt film 102a of the single crystal of a field (100) (001). For this reason, the remanence value  $P_r$  of PZT film 103a of the single crystal of an ideal (001) field can be acquired. Moreover, the remanence ratio of a hysteresis curve is excellent and the SN ratio at the time of polarization reversal is also high. Furthermore, the saturation characteristics over the voltage of a hysteresis curve can also be well driven by the low battery. However, it is difficult to manufacture the substrate which consists the substrate of an area equivalent to a 6 inch wafer of MgO at cost equivalent to Si substrate. For this reason, there is a trouble that it is difficult to use it industrially.

[0011] While this invention can be made in view of this trouble, its remanence value can be high, the remanence ratio of a hysteresis curve can be excellent and the SN ratio at the time of polarization reversal can drive by the low battery highly, it aims at offering the manufacture method of the ferroelectric random-access memory and ferroelectric random-access memory which can be manufactured by the low cost with the degree of low temperature.

[0012]

[Means for Solving the Problem] The ferroelectric random-access memory concerning this invention has the ferroelectric film which has composition containing  $PbxZr(1-y)Ti_yO_3$ , and is characterized by carrying out orientation of the polarization shaft of 10% or more of crystal grain perpendicularly to the front face of the aforementioned ferroelectric film among the crystal grain of the aforementioned ferroelectric film. The rate of the orientation of a polarization shaft is computed by the integrated intensity ratio of the peak of an X diffraction.

[0013] In this case, the value of 0.9 or 1.3, and y of the value of x is 0.3 or 0.7, and, as for the thickness of the aforementioned ferroelectric film, it is desirable that it is 500 or 5000Å.

[0014] other ferroelectric random-access memory concerning this invention --  $PbxZr(1-y)$  -- it has the ferroelectric film which has composition containing  $Ti_yO_3$  and Li, and is characterized by carrying out orientation of the polarization shaft of 10% or more of crystal grain perpendicularly to the front face of the aforementioned ferroelectric film among the crystal grain of the aforementioned ferroelectric film

[0015] In this case, the value of 0.9 or 1.3, and y of the value of x is 0.3 or 0.7, and while the thickness of the aforementioned ferroelectric film is 500 or 5000Å, it is desirable [ the addition of Li ] that it is [ 0.2 or 20 mol ] %.

[0016] In this invention, it is desirable that the crystal grain which is the field where a lower electrode is formed in the inferior-surface-of-tongue side of the aforementioned ferroelectric film, the aforementioned lower electrode consists of material whose lattice constant is  $3.9 \times 0.4\text{Å}$  or  $5.4 \times 0.5\text{Å}$ , and a front face contains a lattice constant among the crystal grain of the aforementioned whole lower electrode is 10% or more.

[0017] For example, thickness is 200 or 3000Å and it is desirable that the crystal grain which carried out orientation to the field (100) among the crystal grain of the aforementioned whole lower electrode is 10% or more while the aforementioned lower electrode consists of Pt or Ir.

[0018] Furthermore, it is desirable that the buffer layer by which orientation was carried out is formed in a field at the side (001) in which the aforementioned ferroelectric film of the aforementioned lower electrode is not formed, for example, the aforementioned buffer layer is  $CeO_2$ .

[0019] The manufacture method of the ferroelectric random-access memory concerning this invention is characterized by having the process which a field (001) is made to carry out orientation and forms a

buffer layer in it, the process which forms the lower electrode whose crystal grain which carried out orientation to the field (100) is 10% or more among the crystal grain of the whole lower electrode on the aforementioned buffer layer, and the process which forms a ferroelectric film on the aforementioned lower electrode.

[0020] In this case, as for the aforementioned ferroelectric film, it is desirable to contain Li.

[0021] In this invention, when the polarization shaft of 10% or more of crystal grain carries out orientation perpendicularly to the front face of a ferroelectric film among the crystal grain of a ferroelectric film, the amount of spontaneous polarization increases and a remanence value becomes high. For this reason, the remanence ratio of a hysteresis curve is excellent, i.e., the SN ratio at the time of polarization reversal becomes high, and it can drive by the low battery.

[0022]

[Embodiments of the Invention] Hereafter, the manufacture method of of the ferroelectric random-access memory and ferroelectric random-access memory concerning the example of this invention is explained in detail with reference to an attached drawing. Drawing 1 is the cross section showing the ferroelectric random-access memory concerning the example of this invention.

[0023] In this example, as shown in drawing 1, SiO<sub>2</sub> film 2 is formed on the semiconductor substrate 1 which consists of Si. On this SiO<sub>2</sub> film 2, CeO<sub>2</sub> film with which orientation of the front face was carried out to the field (001) is formed as a buffer layer 3. On this buffer layer 3, orientation of the front face is mainly (111) carried out as a lower electrode 4 in a field and a field (100), and Pt film this crystal grain of whose the front face of crystal grain is 10% or more in a field (100) among the crystal grain of the lower electrode 4 is formed. The PZT film 5 is formed on this lower electrode 4. 10% or more of fields where orientation of the front face is mainly (001) carried out to a field and a field (111), and this PZT film 5 includes a polarization shaft in these crystal faces (001) exists. That is, orientation of the polarization shaft of 10% or more of crystal grain is perpendicularly carried out to the PZT film 5 among the crystal grain of the front face of the PZT film 5. On this PZT film 5, Pt film by which the main orientation was carried out is formed in the field as an up electrode 6 (111).

[0024] Next, operation of the ferroelectric random-access memory of above-mentioned composition is explained with reference to drawing 2. It is the graphical representation in which drawing 2's taking a polarization value along a vertical axis, taking electric field along a horizontal axis, and showing the hysteresis of ferroelectric random-access memory.

[0025] If the amount of polarization is made to increase along with the arrow in drawing as shown in drawing 2 when electric field are impressed from D points, a polarization value will become zero by F points. They are the electric field which call these F points anti-electric field, and become the standard which carries out polarization reversal. And in the B point whose electric field are E<sub>max</sub>, a polarization value will hardly increase. The polarization value of this B point is called saturation part extremal value P<sub>max</sub>. Then, electric field are impressed to a minus side and electric field are returned to zero. At this time, a polarization value does not become zero but has a certain value. This value is called remanence value P<sub>r</sub>. Furthermore, if electric field are impressed to a minus side, D points which show the saturation part extremal value by the side of minus will be reached. Thereby, a hysteresis curve is formed.

Moreover, in this ferroelectric random-access memory, as shown in drawing 2, the following formula 1 can show an SN ratio.

[0026]

[Equation 1]  $SN\ ratio = P_r / (P_{max} - P_r)$

[0027] Therefore, in order to raise an SN ratio, it is necessary to enlarge the value of the remanence value P<sub>r</sub>.

[0028] In this example, the remanence value P<sub>r</sub> becomes high by carrying out orientation of the polarization shaft of 10% or more of crystal grain perpendicularly to the front face of the PZT film 5 among the crystal grain of the front face of the PZT film 5. For this reason, the SN ratio at the time of polarization reversal becomes high. Moreover, since the remanence value P<sub>r</sub> becomes high, the remanence ratio of a hysteresis curve is excellent. In addition, a field including this polarization shaft (001) cannot make the remanence value P<sub>r</sub> high enough at 10% or less. For this reason, orientation of

the field (001) is carried out 10% or more among the crystal grain of the front face of the PZT film 5. That is, orientation of the polarization shaft of 10% or more of crystal grain is perpendicularly carried out to the PZT film 5 among the crystal grain of the front face of the PZT film 5.

[0029] in addition, this example -- setting -- the PZT film 5 -- Li -- 1 or 20-mol% -- it can also consider as the composition to add. When this Li is added, a leakage-current value can be made small.

[0030] Next, the manufacture method of the ferroelectric random-access memory concerning this example is explained in detail with reference to drawing 1. First, for example, thickness forms SiO<sub>2</sub> film 2 which is 5000Å in the front face of the semiconductor substrate 1 which consists of Si. Next, after it uses CeO<sub>2</sub> target as a target and a degree of vacuum, for example, carries out evacuation of the vacuum chamber of a sputtering system to  $2.0 \times 10^{-6}$  Torr, O<sub>2</sub> gas introduces [ Ar gas of 5mTorr ] 20% of mixed gas into a vacuum chamber 80%. The thickness which temperature of the semiconductor substrate 1 was made [ thickness ] into 100 or 700 degrees C, and made the front face carry out orientation of the field (001) as a buffer layer 3 on this SiO<sub>2</sub> film 2 by RF spatter forms CeO<sub>2</sub> film which is 1000Å.

[0031] Next, after it uses Pt target as a target and a degree of vacuum, for example, carries out evacuation of the vacuum chamber of a sputtering system to  $2.0 \times 10^{-6}$  Torr, 100% of Ar gas of 5mTorr is introduced into a vacuum chamber. By RF spatter, temperature of the semiconductor substrate 1 is made into 700 degrees C, and Pt film whose thickness is 1000Å is formed as a lower electrode 4 on this buffer layer 3. At this time, orientation of the Pt film is automatically carried out on CeO<sub>2</sub> film made [ the field (001) ] to carry out orientation. For this reason, the crystal grain which carries out orientation to a field (100) among the crystal grain of the front face of Pt film can be obtained 10% or more.

[0032] Next, the sol Ringer's injection which has composition of a desired ferroelectric is used as the solution of 10% of the weight of concentration, and spin coating is carried out for 10 seconds at the rotational frequency of 3000rpm on the lower electrode 4. And it prebakes for 10 minutes at 400 degrees C. Henceforth, spin coating and prebaking are repeated 4 times. Next, for example, annealing of 1 hour is performed at the temperature of 600 degrees C, and the PZT film 5 whose thickness is 2000Å is formed. At this time, since the PZT film 5 is formed in the field (100) of Pt film, orientation of it is carried out to nature. For this reason, the crystal grain which carries out orientation to a field (001) among the crystal grain of the front face of the PZT film 5 can be obtained 10% or more.

[0033] Next, after it uses Pt target as a target as an up electrode 6 and a degree of vacuum carries out evacuation of the vacuum chamber of a sputtering system to  $2.0 \times 10^{-6}$  Torr on this PZT film 5, 100% of Ar gas of 5mTorr is introduced into a vacuum chamber. By RF spatter, temperature of the semiconductor substrate 1 is made into 700 degrees C, and Pt film whose thickness is 1000Å is formed as an up electrode 6 on this PZT film 5. Thereby, ferroelectric random-access memory can be manufactured.

[0034] this example -- setting -- the PZT film 5 -- Li -- 0.2 or 20-mol% -- it can add. In addition, less than [ 0.2mol% ], as for this addition of Li, an annealing temperature becomes high. On the other hand, if the addition of Li exceeds 20-mol%, an SN ratio will fall and a leakage-current value will rise. For this reason, the addition of Li is made into 0.2 or 20-mol%.

[0035] Moreover, as compared with the thing of only the PZT film 5, an annealing temperature falls by adding Li. for example, -- although it was 650 degrees C in this example -- Li -- 1 or 20-mol% -- in what was added, it is 550 degrees C. Furthermore, even if an annealing temperature compares with a SBT film, it can be performed the degree of low temperature, can be accumulated, and it can suppress the influence by the heat at the time of manufacture.

[0036] Moreover, in this example, the crystal grain which orientation of the formed Pt film is automatically carried out, and carries out orientation to a field (100) among the crystal grain of the front face of Pt film can be obtained 10% or more by forming Pt film as a lower electrode 4 on the buffer layer 3 which consists of CeO<sub>2</sub> film to which orientation of the field (001) was carried out. For this reason, since the field of the PZT film 5 formed on the lower electrode 4 is also formed in the field (100) of Pt film, orientation of it is carried out to nature. By this, the crystal grain by which orientation was carried out to the field (001) by the integrated intensity ratio of the peak of an X diffraction among the

crystal grain of the front face of the PZT film 5 can be obtained 10% or more. Therefore, the high remanence value  $P_r$  can be acquired. Moreover, a hysteresis curve is also excellent in a remanence ratio, and the SN ratio at the time of polarization also becomes high. Furthermore, the saturation characteristics over the voltage of a hysteresis curve can be excellent, and it can drive by the low battery.

[0037] Furthermore, in this example, although thickness of the PZT film 5 was made into 2000Å, it is 1000 or 3000Å that it is 500 or 5000Å desirable still more preferably. Moreover, the lower electrode 4 is not limited to Pt film, and also let it be Ir film. Although thickness of this lower electrode 4 was made into 1000Å, 200 or 3000Å are 500 or 2000Å desirable still more preferably. It is desirable for the field (100) to carry out orientation of any lower electrode 4 10% or more. Furthermore, if a lattice constant is  $3.9 \times 0.4\text{Å}$  or  $5.4 \times 0.5\text{Å}$  as a material of the lower electrode 4, it will not be limited to an above-mentioned example.

[0038]

[Example] Hereafter, the ferroelectric random-access memory of the structure of the example of comparison shown in the ferroelectric random-access memory of the structure of the example shown in drawing 1 and drawing 6, or 8 about the example of this invention is produced, and the result which compared both property is explained.

[0039] The ferroelectric random-access memory of a PZT film which has composition of  $\text{PbZr}_{0.52}\text{Ti}_{0.48}$  by the method of the example of the 1st example this invention was produced. As example No.1, thickness formed the PZT film which is 2000Å on Pt film with which the main orientation of the field (001) is carried out. On the other hand, thickness formed the PZT film which is 2000Å as example No. of comparison 20 on Pt film with which the main orientation of the field (111) is carried out. The hysteresis curve was investigated for this example No.1 and example No. of comparison 20, respectively. This result is shown in drawing 3. It is the graphical representation in which drawing 3's taking a polarization value ( $2P_r$ ) along a vertical axis, taking electric field along a horizontal axis, and showing the hysteresis of ferroelectric random-access memory. A solid line shows example No.1 among drawing 3, and a dashed line shows example No. of comparison 20.

[0040] Since example No.1 included in the range of this invention formed the PZT film on Pt film by which the main orientation is carried out to the field (001) as shown in drawing 3, as for the PZT film, the orientation of the front face became is easy to be carried out to a field (001). For this reason, it became the hysteresis curve excellent in the remanence ratio. Moreover, the SN ratio was also able to be made high. On the other hand, since example No. of comparison 20 formed the PZT film on Pt film with which the main orientation of the field (111) is carried out, as for the PZT film, orientation became is easy to be carried out to a field (111). For this reason, in order that polarization might not act effectively to electric field, the remanence value  $P_r$  was low, the remanence ratio became small, and the SN ratio became a low thing.

[0041] The rate of orientation of the field (001) of the front face of the PZT film which has composition of  $\text{PbZr}_{0.52}\text{Ti}_{0.48}$  by the method of the example of the 2nd example this invention was changed, and ferroelectric random-access memory was produced. About these ferroelectric random-access memory, driver voltage measured the remanence value  $P_r$ , SN ratio, and saturation voltage in  $\times 1.5\text{V}$ . Driver voltage made the saturation electrode the voltage which can acquire 90% of the remanence value  $P_r$  in  $\times 5\text{V}$ .

[0042] In addition, the desired value of the remanence value  $P_r$  is  $10\text{microC}/\text{cm}^2$ , the desired value of an SN ratio is 5, and the desired value of a saturation voltage is  $1.5\text{V}$ . these results are looked like [ Table 1 and drawing 4 ], and are shown Drawing 4 takes the rate of orientation of the field (001) of a PZT film on a vertical axis along the remanence value [ in /  $\times 1.5\text{V}$  / in driver voltage ]  $P_r$ , an SN ratio and a saturation voltage, and a horizontal axis, and the rate of orientation and driver voltage of a field (001) of a PZT film are the graphical representation showing a relation with the remanence value  $P_r$ , SN ratio, and saturation voltage in  $\times 1.5\text{V}$ . As for  $\diamond$ , an SN ratio and  $\times$  show  $P_r$  among drawing 4,  $\times$  shows a saturation voltage, further,  $\diamond$  shows the desired value of  $P_r$  and, as for  $\times$ , the desired value of an SN ratio and  $\times$  show the desired value of a saturation voltage.

[0043]

[Table 1]

	No.	PZT(001) 配向率(%)	P <sub>r</sub> ( $\mu$ C/cm <sup>2</sup> )	P <sub>r</sub> / (P <sub>max</sub> - P <sub>r</sub> )	飽和電圧 (V)
実施例	2	10	23.4	7	1.5
	3	20	27	9	1.5
	4	50	36	18	1.5
	5	100	46	50	1.5
比較例	21	1	8	4	4
	22	5	9	4.5	3

[0044] As shown in the above-mentioned table 1 and drawing 4, the remanence value P<sub>r</sub>, an SN ratio, and a saturation electrode were able to satisfy desired value. [ in / \*\*1.5V / 5 / example No.2 or / in driver voltage ] On the other hand, since the rate of orientation of the field (001) of a PZT film was under the range of this invention, as for example No.of comparison 21, or 22, the remanence value P<sub>r</sub>, an SN ratio, and a saturation voltage were not able to satisfy desired value. [ in / \*\*1.5V / in driver voltage ]

[0045] the PZT film which has composition of PbZr<sub>0.52</sub>Ti<sub>0.48</sub> by the method of the example of the 3rd example this invention -- Li -- 0 or 25-mol% -- it added and ferroelectric random-access memory was produced About these ferroelectric random-access memory, an SN ratio, a leakage-current value, and driver voltage measured the leakage-current value and the minimum annealing temperature in \*\*5V. [ in / \*\*1.5V / in driver voltage ]

[0046] In addition, the desired value of an SN ratio is 5 and the desired value of a leakage-current value [ in / \*\*1.5V and \*\*5V / in driver voltage ] is 1microA/cm<sup>2</sup>. these results are looked like [ Table 2 and drawing 5 ], and are shown Drawing 5 takes the addition of Li on a vertical axis along an SN ratio [ in / \*\*1.5V / in driver voltage ], a leakage-current value, a leakage-current value / in / \*\*5V / in driver voltage ] and the minimum annealing temperature, and a horizontal axis, and it is the graphical representation showing the relation between the addition of Li, an SN ratio / in / \*\*1.5V / in driver voltage ], a leakage-current value, and a leakage-current value / in / \*\*5V / in driver voltage ]. A leakage-current value [ in / \*\*1.5V / <> among drawing 5, and / in O ], a leakage-current value / in / \*\*5V / in - ], and \*\* show the minimum annealing temperature, and, as for <>, the desired value of an SN ratio and \*\* show the desired value of a leakage-current value further. / an SN ratio

[0047]

[Table 2]

	No.	Li 添加量 (mol%)	P <sub>r</sub> / (P <sub>max</sub> - P <sub>r</sub> )	リーク電流 ( $\mu$ A/cm <sup>2</sup> )		最低アニール 温度(°C)
				( $\pm$ 1.5V)	( $\pm$ 5V)	
実施例	6	1	18	0.1	0.4	550
	7	10	17	0.1	0.3	550
	8	20	15	0.3	0.6	550
比較例	23	0	18	0.3	0.9	650
	24	25	2	1	5	550

[0048] As shown in the above-mentioned table 2 and drawing 5, example No.6 or 8 was that with which an SN ratio, a leakage-current value, and driver voltage are satisfied of the desired value of the leakage-

current value in \*\*5V. [ in / \*\*1.5V / in driver voltage ]

[0049] On the other hand, since the addition of Li is under the range of this invention, although example No. of comparison 23 satisfy an SN ratio [ in / \*\*1.5V / in driver voltage ], a leakage-current value, and the desired value of a leakage-current value / in / \*\*5V / in driver voltage ], the minimum annealing temperature has become high. Since, as for example No. of comparison 24, the addition of Li is over the range of this invention, an SN ratio, a leakage-current value, and driver voltage have exceeded the desired value of the leakage-current value in \*\*5V. [ in / \*\*1.5V / in driver voltage ]

[0050] The ferroelectric random-access memory which performs a sputter on the sputtering conditions shown in Table 3 by the method of the example of the 4th example this invention, and is shown in Table 4 or 11 was produced. In addition, in this example, it formed on Si substrate of 0.6mm of board thickness except for example No. of comparison 26 on SiO<sub>2</sub> film whose thickness is 5000Å. The front face whose lattice constant board thickness is 4.2Å in 0.8mm formed example No. of comparison 26 on the MgO single crystal substrate of a field (100).

[0051] The remanence value Pr, a saturation voltage, an SN ratio, productivity, and the leakage-current value were measured about the ferroelectric random-access memory shown in these Table 4 or 9.

[0052] Measurement of the remanence value Pr was performed by having impressed the driver voltage of \*\*5, \*\*3V, and 1.5 [ \*\*], and the reference value was made into 10microC/cm<sup>2</sup>.

[0053] The saturation voltage considered as 90% of value of the remanence Pr which can be acquired by the driver voltage of \*\*5V, and made the reference value less than [ 1.5V ].

[0054] The SN ratio impressed the driver voltage of \*\*5, \*\*3V, and 1.5 [ \*\*], performed it, set the reference value to 2, and made it five or more preferably.

[0055] Productivity observed the membrane formation state on Si substrate. Criteria made good what has a good membrane formation state.

[0056] Measurement of a leakage current was performed by having impressed the driver voltage of \*\*5, \*\*3V, and 1.5 [ \*\*], and the reference value was made into 10microA/cm<sup>2</sup>. These results are shown in Tables 10 and 11.

[0057]

[Table 3]

サンプル No.	CeO <sub>2</sub> 成膜 温度(℃)	CeO <sub>2</sub> (001) 配向(%)	Pt 成膜 温度(℃)	Pt(001) 配向(%)	PTT 温度	PZT(001) 配向(%)
A	300	10	700	10	700	5
B	450	20	700	20	700	10
C	700	50	700	50	700	20
D	100	5	700	5	700	5

[0058]

[Table 4]

		実施例 No. 9	実施例 No. 10
上部電極	上部電極材料	Pt	Pt
	上部電極膜厚(Å)	1000	1000
強誘電体	強誘電体材料	$\text{PbZr}_{0.52}\text{Ti}_{0.48}$	$\text{PbZr}_{0.52}\text{Ti}_{0.48}$
	格子定数(Å)	3.9	3.9
	成膜法	スパッタ	スパッタ
	成膜温度(°C)	650~750	650~750
	膜厚(Å)	1000	1000
	分極軸配向割合	(001)10%	(001)20%
下部電極	下部電極材料	Pt	Pt
	格子定数(Å)	3.9	3.9
	下部電極膜厚(Å)	1000	1000
	(100)面配向割合	10%	20%
バツア層	バツア層材料	$\text{CeO}_2$	$\text{CeO}_2$
	格子定数(Å)	5.2	5.2
	成膜法(スパッタ No.)	A	B
	バツア層膜厚(Å)	200	200
	(001)面配向割合	(001)10%	(001)20%

[0059]

[Table 5]



		実施例 No. 1 1	実施例 No. 1 2
上部電極	上部電極材料	P t	I r
	上部電極膜厚(Å)	1000	1000
強誘電体	強誘電体材料	$\text{PbZr}_{0.52}\text{Ti}_{0.48}$	$\text{PbZr}_{0.52}\text{Ti}_{0.48}$
	格子定数(Å)	3.9	3.9
	成膜法	パルス	パルス
	アニール温度(°C)	650~750	650~750
	膜厚(Å)	1000	1000
	分極軸配向割合	(001)50%	(001)50%
下部電極	下部電極材料	P t	I r
	格子定数(Å)	3.9	3.9
	下部電極膜厚(Å)	1000	1000
	(100)面配向割合	50%	50%
バッド層	バッド層材料	$\text{CeO}_2$	$\text{CeO}_2$
	格子定数(Å)	5.2	5.2
	成膜法(スパッタ No.)	C	C
	バッド層膜厚(Å)	200	200
	(001)面配向割合	(001)50%	(001)50%

[0060]

[Table 6]

		実施例 No. 1 3	実施例 No. 1 4
上部電極	上部電極材料	P t	P t
	上部電極膜厚(Å)	1000	1000
強誘電体	強誘電体材料	$\text{PbZr}_{0.52}\text{Ti}_{0.48}+\text{Li}1\%$	$\text{PbZr}_{0.52}\text{Ti}_{0.48}+\text{Li}1\%$
	格子定数(Å)	3.9	3.9
	成膜法	ゾルゲル	ゾルゲル
	7- $\pi$ 温度(°C)	550~700	550~700
	膜厚(Å)	1000	1000
	分極軸配向割合	(001)20%	(001)50%
下部電極	下部電極材料	P t	P t
	格子定数(Å)	3.9	3.9
	下部電極膜厚(Å)	1000	1000
	(100)面配向割合	20%	50%
バツフア層	バツフア層材料	$\text{CeO}_2$	$\text{CeO}_2$
	格子定数(Å)	5.2	5.2
	成膜法(バツフア No.)	B	C
	バツフア層膜厚(Å)	200	200
	(001)面配向割合	(001)20%	(001)50%

[0061]

[Table 7]

		実施例 No. 1 5	実施例 No. 1 6
上部電極	上部電極材料	P t	P t
	上部電極膜厚(Å)	1000	1000
強誘電体	強誘電体材料	$\text{PbZr}_{0.62}\text{Ti}_{0.48} + \text{Li}10\%$	$\text{PbZr}_{0.52}\text{Ti}_{0.48} + \text{Li}20\%$
	格子定数(Å)	3.9	3.9
	成膜法	ゾルゲル	ゾルゲル
	アニール温度(℃)	550～700	550～650
	膜厚(Å)	1000	1000
	分極軸配向割合	(001)50%	(001)50%
下部電極	下部電極材料	P t	P t
	格子定数(Å)	3.9	3.9
	下部電極膜厚(Å)	1000	1000
	(100)面配向割合	50%	50%
バツフア層	バツフア層材料	$\text{CeO}_2$	$\text{CeO}_2$
	格子定数(Å)	5.2	5.2
	成膜法	C	C
	バツフア層膜厚(Å)	200	200
	(001)面配向割合	(001)50%	(001)50%

[0062]

[Table 8]

		実施例 No.1 7	実施例 No.1 8
上部電極	上部電極材料	I r	I r
	上部電極膜厚(Å)	1000	1000
強誘電体	強誘電体材料	$\text{PbZr}_{0.52}\text{Ti}_{0.48} + \text{Li}1\%$	$\text{PbZr}_{0.40}\text{Ti}_{0.60}$
	格子定数(Å)	3.9	3.9
	成膜法	ゾルゲル	ゾルゲル
	成膜温度(°C)	550~700	650~700
	膜厚(Å)	1000	1000
	分極軸配向割合	(001)50%	(001)50%
下部電極	下部電極材料	I r	I r
	格子定数(Å)	3.9	3.9
	下部電極膜厚(Å)	1000	1000
	(100)面配向割合	50%	50%
バツフア層	バツフア層材料	$\text{CeO}_2$	$\text{CeO}_2$
	格子定数(Å)	5.2	5.2
	成膜法	C	C
	バツフア層膜厚(Å)	200	200
	(001)面配向割合	(001)50%	(001)50%

[0063]

[Table 9]

		実施例 No. 1 9	比較例 No. 2 5
上部電極	上部電極材料	I r	P t
	上部電極膜厚(Å)	1000	1000
強誘電体	強誘電体材料	$\text{PbZr}_{0.49}\text{Ti}_{0.51}\text{+Li1\%}$	$\text{PbZr}_{0.52}\text{Ti}_{0.48}$
	格子定数(Å)	3.9	3.9
	成膜法	ゾルゲル	ゾルゲル
	アニール温度(°C)	550~700	650~750
	膜厚(Å)	1000	1000
	分極軸配向割合	(001)50%	(001)0%、 (111)メイン
下部電極	下部電極材料	I r	P t
	格子定数(Å)	3.9	3.9
	下部電極膜厚(Å)	1000	1000
	(100)面配向割合	50%	0%、(111)メイン
バッド層	バッド層材料	$\text{CeO}_2$	—
	格子定数(Å)	5.2	—
	成膜法	C	—
	バッド層膜厚(Å)	200	—
	(001)面配向割合	(001)50%	—

[0064]

[Table 10]

		比較例 No. 2 6	比較例 No. 2 7
上部電極	上部電極材料	P t	P t
	上部電極膜厚(Å)	1000	1000
強誘電体	強誘電体材料	SrBiTa <sub>2</sub> O <sub>9</sub>	PbZr <sub>0.52</sub> Ti <sub>0.48</sub>
	格子定数(Å)	—	3.9
	成膜法	パルス	MOCVD
	成膜温度(°C)	750~850	650~750
	膜厚(Å)	1000	1000
	分極軸配向割合	—	(001)100%
下部電極	下部電極材料	P t	P t
	格子定数(Å)	3.9	3.9
	下部電極膜厚(Å)	1000	1000
	(100)面配向割合	0%、(111)メイン	100%
バッファ層	バッファ層材料	—	—
	格子定数(Å)	—	—
	成膜法	—	—
	バッファ層膜厚(Å)	—	—
	(001)面配向割合	—	—

[0065]

[Table 11]

		比較例 No. 2 8	比較例 No. 2 9
上部電極	上部電極材料	P t	P t
	上部電極膜厚(Å)	1000	1000
強誘電体	強誘電体材料	$\text{PbZr}_{0.52}\text{Ti}_{0.48}$	$\text{PbZr}_{0.52}\text{Ti}_{0.48} + \text{Li25}\%$
	格子定数(Å)	3.9	3.9
	成膜法	ゾルゲル	ゾルゲル
	アニール温度(°C)	650~750	550~650
	膜厚(Å)	1000	1000
	分極軸配向割合	(001)5%	(001)50%
下部電極	下部電極材料	P t	P t
	格子定数(Å)	3.9	3.9
	下部電極膜厚(Å)	1000	1000
	(100)面配向割合	5%	50%
バフ層	バフ層材料	$\text{CeO}_2$	$\text{CeO}_2$
	格子定数(Å)	5.2	5.2
	成膜法	D	C
	バフ層膜厚(Å)	200	200
	(001)面配向割合	(001)5%	(001)50%

[0066]

[Table 12]

	No.	P <sub>r</sub> (μC/cm <sup>2</sup> )			飽和電圧
		(±15V)	(±3V)	(±5V)	
実 施 例	9	26	25	23.4	±15V
	10	30	29	27	±15V
	11	40	38	36	±15V
	12	38	37	35	±15V
	13	29	28	26.1	±15V
	14	39	37	35.1	±15V
	15	30	28	27	±15V
	16	25	24	22.5	±15V
	17	38	36	34.2	±15V
	18	39	36	35.2	±15V
	19	38	36	35	±15V
比 較 例	25	20	16	8	±3V以上
	26	5	5	4.5	±15V
	27	50	50	46	±15V
	28	21	19	9	±3V以上
	29	20	18	15	±3V

[0067]

[Table 13]



	No.	Pr/(Pmax·Pr)			生産性	リーク電流( $\mu$ A/cm <sup>2</sup> )	
		( $\pm 1.5$ V)	( $\pm 3$ V)	( $\pm 5$ V)		( $\pm 1.5$ V)	( $\pm 5$ V)
実施例	9	3	5	7	良	0.3	0.8
	10	5	7	9	良	0.2	0.7
	11	10	13	18	良	0.3	0.9
	12	10	13	18	良	0.4	0.9
	13	5	7	9	良	0.1	0.5
	14	10	13	18	良	0.1	0.4
	15	9	11	17	良	0.1	0.3
	16	8	10	15	良	0.3	0.6
	17	11	14	19	良	0.2	0.5
	18	13	15	20	良	0.2	0.5
	19	11	14	19	良	0.2	0.5
比較例	25	1	2	4	良	0.4	1
	26	2.5	5	9	良	0.2	0.7
	27	50 以上	50 以上	50 以上	困難	0.3	0.9
	28	1	2.2	4.5	良	0.4	0.7
	29	5	8	2	良	1.0	5

[0068] As shown in the above-mentioned tables 12 and 13, example No.9 included in the range of this invention or 19 could satisfy the reference value about all the remanence value Pr, a saturation voltage, SN ratios, the productivity, and leakage-current values, and was able to obtain the good result.

[0069] On the other hand, example No. of comparison 25 or 29 could not satisfy a reference value about the remanence value Pr, a saturation voltage, an SN ratio, productivity, and a leakage-current value, and was not able to obtain a good result.

[0070] Since the orientation side of a field (111) of a PZT film was main, example No. of comparison 25 had the remanence value [ in /  $\times 1.5$ V / in driver voltage ] Pr, and the low SN ratio. For this reason, in this driver voltage, the drive was difficult. Moreover, a saturation voltage and a leakage-current value were not able to satisfy a reference value, either. Furthermore, the remanence ratio also became scarce.

[0071] Since a ferroelectric film was not a PZT film but a SBT film, while example No. of comparison 26 had the high annealing temperature, the remanence value Pr became low.

[0072] Since example No. of comparison 27 were formed on the MgO substrate, productivity became scarce. For this reason, it is not suitable for industrial production.

[0073] Since the rate of orientation of the field (001) of a PZT film was 5%, example No. of comparison 28 had the remanence value [ in /  $\times 1.5$ V / in driver voltage ] Pr, and the low SN ratio. For this reason, in this driver voltage, the drive was difficult. Moreover, a saturation voltage and a leakage-current value were not able to satisfy a reference value, either. Furthermore, the remanence ratio also became scarce.

[0074] Since the addition of Li was 25-mol%, example No. of comparison 29 had the low SN ratio [ in /  $\times 1.5$ V / in driver voltage ]. For this reason, the loop of a hysteresis curve also collapsed and the drive was difficult in this driver voltage. Moreover, a saturation voltage and a leakage-current value were not able to satisfy a reference value, either.

[0075]

[Effect of the Invention] As explained in full detail above, when the polarization shaft of 10% or more of crystal grain carries out orientation perpendicularly to the front face of a ferroelectric film in this

invention, the amount of spontaneous polarization increases and a remanence value becomes high. For this reason, the remanence ratio of a hysteresis curve is excellent, i.e., the SN ratio at the time of polarization reversal becomes high, and it can drive by the low battery.

[0076] Moreover, by carrying out orientation of the field (100) 10% or more, forming a lower electrode on the buffer layer to which orientation of the field (001) was carried out, and forming a ferroelectric film on this, orientation is carried out automatically and the polarization shaft of crystal grain can carry out orientation perpendicularly to the front face of a ferroelectric film among the crystal grain of a ferroelectric film 10% or more. For this reason, the high remanence value  $P_r$  can be acquired.

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[Translation done.]